



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 881 201 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
18.09.2002 Bulletin 2002/38

(51) Int Cl.7: **C07C 17/37, C07C 19/12**

(21) Application number: **98109067.3**

(22) Date of filing: **19.05.1998**

(54) Process for preparing HCFC-123

Verfahren zur Herstellung von HCFC-123

Procédé de préparation du HCFC-123

(84) Designated Contracting States:
BE DE FR GB IT NL

(30) Priority: **27.05.1997 IT MI971237**

(43) Date of publication of application:
02.12.1998 Bulletin 1998/49

(73) Proprietor: **Ausimont S.p.A.**
20121 Milano (IT)

(72) Inventors:
• **Cuzzato, Paolo**
Ponzano Veneto, Treviso (IT)

• **Rinaldi, Francesco**
Padova (IT)
• **Bragante, Letazio**
Due Carrare, Padova (IT)

(74) Representative: **Sama, Daniele, Dr. et al**
Sama Patents,
Via G.B. Morgagni, 2
20129 Milano (IT)

(56) References cited:
EP-A- 0 569 832 **WO-A-92/02476**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 881 201 B1

Description

[0001] The present invention relates to the synthesis of $\text{CF}_3\text{-CHCl}_2$ (HCFC-123) having a very low content of undesired unsaturated components.

[0002] More specifically the present invention relates to the use of a specific process for preparing HCFC-123 leading to the desired product with very low amounts of $\text{CF}_3\text{-CF=CCl-CF}_3$ (CFC-1317) and $\text{CF}_3\text{-CH=CCl-CF}_3$ (HCFC-1326), said process having a selectivity in useful products not lower than 98%.

[0003] HCFC-123 is an hydrochlorofluorocarbon (HCFC) having a low ODP (low impact on the ozone layer reduction) whose production is therefore of remarkable industrial interest, for instance as foaming agent for polymeric foams, as fire-extinguishing agent and as refrigerant in cooling plants, etc.

[0004] For these reasons the HCFC-123 purity requirements must be extremely high: in particular it is desirable that it has a content not higher than 10 ppm of unsaturated compounds (collectively indicated hereinafter by the name of "olefins"), as $\text{CF}_2\text{=CCl}_2$ (CFC-1112a), HCFC-1326 and HFC-1317. These olefinic compounds are indeed toxic and unstable. If the processes leading to the formation of HCFC-123 bring to an olefin content over the above limit, other phases leading to the reduction of said compounds must be used in the industrial plants.

[0005] It is important to note that the HCFC-123 separation from these olefins by fractional distillation is often extremely difficult, therefore it is almost impossible to obtain the above mentioned purity in industrial scale. Consequently, remarkable research efforts have been made to succeed in finding an effective method to purify HCFC-123 at industrial level.

[0006] For instance, it is possible to turn said olefins into quite harmless saturated products (and/or more easily separable). In JP 04/360,844, the catalytic hydrogenation of CFC-1317 contained in HCFC-123 by means of molecular hydrogen on a platinum catalyst is described.

[0007] In JP 05/32,567 the use of molecular chlorine on active carbon by chlorination of $\text{CF}_2\text{=CCl}_2$ (CFC-1112a) contained in the HCFC-123 is described, thus obtaining HCFC-123 with a residual content of olefins of 18 ppm.

[0008] In USP 5,367,103 the use of molecular fluorine to remove CFC-1112a from HCFC-123 is described.

[0009] Another method often described in the art is the selective adsorption of olefins by means of suitable adsorbents. For instance in EP 511,612 the HCFC-1326 is removed from HCFC-123 by adsorption on zeolite Y.

[0010] Therefore each process needs at least a supplementary step in the contaminated HCFC-123 treatment, sometimes neither sufficient to obtain the desired purity.

[0011] Moreover, the HCFC-123, commonly produced from perchloro ethylene and HF by a fluorination catalyst, see for instance USP 4,967,023, contains remarkable amounts of the so called "asymmetrical" isomers HCFC-123a and 123b, respectively $\text{CF}_2\text{Cl-CFHCl}$ and $\text{CF}_2\text{H-CCl}_2\text{F}$, undesired due to their poor stability, and therefore transformed into more easily separable compounds (see USP 5,414,167) or isomerized to the $\text{CF}_3\text{-CH}_2\text{Cl}$ (HCFC-133a) which is thermodynamically more stable. As it can be seen, also in this process at least a supplementary treatment of the product is required for the reduction of the undesired by products.

[0012] In EP 569832 a dismutation process of HCFC-114 is indicated at a temperature range $150^\circ\text{-}330^\circ\text{C}$ with Cr_2O_3 as catalyst, optionally supported on AlF_3 , yielding a mixture of HCFC-123 with HFC-125 and other by-products. WO 92/02476 deals with an equilibration reaction of HCFC-124 disproportionating to HCFC-123 and HFC-125 at a temperature range $120\text{-}307^\circ\text{C}$ by using a not-supported trivalent chromium catalyst or a supported catalyst selected

among cobalt, copper, iron, manganese, nickel or zinc.

[0013] Therefore it is of remarkable industrial interest to have available a process having a high selectivity, not lower than 98%, to prepare HCFC-123 free as much as possible both from the olefins and from the asymmetric isomers, thus eliminating further additional purification treatments.

[0014] The Applicant has unexpectedly and surprisingly found that it is possible to obtain HCFC-123 containing very small amounts of olefins, lower than 10 ppm, if the process described hereinafter is used.

[0015] It is therefore an object of the present invention a process for preparing HCFC-123 having a content of olefins lower than 10 ppm by dismutation of gaseous CHClF-CF_3 (HCFC-124) by contact with a catalyst which essentially consists of three valence chromium oxide (Cr_2O_3) supported on aluminum fluoride, at temperatures comprised between 180 and 220°C and with contact times between 5-25 sec, preferably 10-20 sec.

[0016] It has been found that the temperature is the most important reaction parameter, while the contact time has comparatively a lower effect.

[0017] The lower is the temperature in the indicated range, the better are the results in terms of global selectivity, while the conversion is obviously better at higher temperatures.

[0018] The HCFC-124 which is used as reactant in the dismutation is produced by perchloroethylene fluorination, therefore it has high production costs. It is therefore necessary that the dismutation process has a selectivity to HCFC-123 and $\text{CHF}_2\text{-CF}_3$ (HFC-125) higher than or equal to 98% to be an industrially and economically acceptable process.

[0019] Moreover, from the environmental point of view it is preferable to have high selectivity since the by-products are mainly formed by CFC of which the dangerous effect on the ozone layer is well known.

[0020] It is well known that the CFCs disposal requires suitable devoted incineration plants.

[0021] As aluminum fluoride, used as support, according to the present invention, it is meant the alumina fluorination product, having a fluorine content not lower than 90%, preferably not lower than 95%, of the stoichiometric. Preferably the granulometry of the support and of its precursor is suitable to be used in fluidized bed.

[0022] The preferred support is the 100% by weight AlF_3 , preferably in the gamma and/or beta structure.

[0023] AlF_3 can also contain the delta structure, generally up to 30% by weight.

[0024] The Cr content in the supported catalyst generally ranges between 1 and 15% by weight, calculated as Cr in the catalyst.

[0025] As chromium oxide supported on AlF_3 it is meant trivalent Cr oxide Cr_2O_3 ; during the activation and the process of the invention, reaches the equilibrium with the reactants, by partial transformation into oxyfluoride, fluoride and oxychloride.

[0026] The catalyst of the invention is particularly suitable to be used in the fluidized bed plants.

[0027] The preferred general procedure for preparing the catalyst consists in impregnating a certain amount of the support with a concentrated solution of a soluble Cr(III) salt, for instance chloride. The volume of the impregnating solution is equal to or lower than the support pore volume, in order to avoid the adhesion among the granules of the same. In particular the catalyst is prepared according to Example 7 of USP 5,345,014, herein incorporated by reference.

[0028] The catalyst of the invention maintains an high activity during the time wherefore it does not require frequent regeneration processes. These are carried out according to the method described in USP 4,967,023, herein incorporated by reference.

[0029] The following examples are given for illustrative purposes but are not limitative of the scope of the present invention.

EXAMPLE 1A - Catalyst preparation

[0030] A sample of aluminum fluoride having granulometry suitable for a fluidized bed is "dry" impregnated with a concentrated aqueous solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, in the range of 492 g of chromium chloride for 1000 g of aluminium fluoride. The so obtained catalyst is calcined at 400°C under nitrogen flow (about 100 NL/h) for 10 hours, then fluorinated at 360°C with anhydrous HF for 24 hours.

EXAMPLE 1B - Dismutation of HCFC-124

[0031] 300 cc of the catalyst of Example 1A are introduced in a 50 mm tubular reactor, electrically heated and equipped with porous septum at the base. At the temperature of 240°C , 273 g/h (2 moles/h) of HCFC-124 are fed to the reactor, thus achieving a contact time equal to about 13 sec. The gases coming out from the reactor are washed in water to remove acidity traces and analyzed by gas chromatography GC with HWD detector (thermoconductibility). The following analysis is representative of the obtained results:

HFC-125	39.8% mole
HCFC-124	25.5
HCFC-123	33.4
Others	1.3

[0032] The HCFC-124 conversion is equal to 74.5% and the global selectivity of the process (CFC-125 + HCFC-123) is of 98%. The amount of olefins (CFC-1112a + HCFC-1326 + CFC-1317) in the reaction products is too small to be directly measured, wherefore the analysis is repeated by gas chromatography/GC-MS mass. The following results are obtained:

CFC-1112a	0.16 ppm
HCFC-1326	< 0.1 ppm
CFC-1317	< 0.1 ppm

EXAMPLE 1C

[0033] The HCFC-124 dismutation of Example 1B is repeated in different temperature conditions and contact times: the relative results are summarized in Table 1.

[0034] It can be noted how there is never a measurable amount of olefins up to the temperature of 280°C , however

at temperatures higher than 220°C the selectivity is equal to or lower than 98%.

EXAMPLE 2

[0035] Example 1B is repeated at 320°C with a HCFC-124 feeding of 1.3 mole/hour, thus achieving a contact time of about 17 sec. The results are reported in the last column of Table 1. As it can be seen, the HCFC-124 conversion increases as well as the olefins content, while the global selectivity of the process decreases.

TABLE 1

Examples	1C	1C	1B	1C	1C	1C	1C	1C	1C	2 comp
Feed 124 mole/h	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.3
Temperature, °C	180	220	240	260	280	300	320	320	320	320
Contact time, sec.	14.5	13.3	12.8	12.3	11.9	11.5	11.1	11.1	11.1	17.1
125 % mole	22.36	27.01	39.80	45.00	50.64	50.19	51.91	51.91	51.91	53.75
124	56.50	47.20	25.53	21.77	18.56	19.12	18.14	18.14	18.14	15.80
133	0.03	0.06	0.16	0.31	0.65	1.06	2.22	2.22	2.22	2.81
114	0.02	0.07	0.10	0.16	0.23	0.44	0.69	0.69	0.69	1.05
123a+b	0.01	0.02	0.02	0.08	0.03	0.03	0.03	0.03	0.03	0.00
123	21.06	25.47	33.36	31.39	27.90	26.24	22.00	22.00	22.00	20.11
110	0.00	0.05	0.68	1.06	0.72	0.60	0.55	0.55	0.55	1.03
Others	0.02	0.11	0.35	0.23	1.27	2.31	4.47	4.47	4.47	5.45
Conv. 124	43.50	52.80	74.47	78.23	81.44	80.88	81.86	81.86	81.86	84.20
Sel. 123+125	1.00	0.99	0.98	0.98	0.96	0.95	0.90	0.90	0.90	0.88
123a+b/123 tot %	0.05	0.07	0.06	0.25	0.10	0.12	0.12	0.12	0.12	0.02
1112a, ppm	n.d.	n.d.	0.16	<0.1	<0.1	n.d.	n.d.	n.d.	n.d.	n.d.
1317, ppm	n.d.	<0.5	<0.1	<0.1	<0.1	<0.5	1	1	1	1.6
1326, ppm	n.d.	<0.5	<0.1	<0.1	<0.1	4.2	9.5	9.5	9.5	11.4
Olefines in 123 ppm	n.d.	<10	<10	<10	<10	16	48	48	48	65

Claims

1. Process for preparing HCFC-123 having an olefin content lower than 10 ppm by dismutation of gaseous HCFC-124 by contact with a catalyst which essentially consists of three valence chromium oxide (Cr_2O_3) supported on

aluminum fluoride, at temperatures comprised between 180 and 220°C, and with contact times between 5-25 sec, wherein said dismutation process has a selectivity of useful products HCFC-123 and HCFC-125 higher than 98%.

2. Process for preparing HCFC-123 according to claim 1, wherein the aluminium fluoride is the alumina fluorination product, with a fluorine content not lower than 90%, preferably not lower than 95%, of the stoichiometric.
3. Process for preparing HCFC-123 according to claims 1 and 2, wherein the support is the 100% by weight AlF_3 in the gamma form.
4. Process for preparing HCFC-123 according to claims from 1 to 3 wherein the chromium oxide is in the presence of oxyfluoride, fluoride and oxychloride.

Patentansprüche

1. Verfahren zur Herstellung von HCFC-123 mit einem Olefingehalt von weniger als 10 ppm durch Dismutation von gasförmigem HCFC-124 durch Kontakt mit einem Katalysator, der im wesentlichen aus dreiwertigem Chromoxid (Cr_2O_3) besteht, das auf Aluminiumfluorid geträgert ist, bei Temperaturen zwischen 180 und 220°C und mit Kontaktzeiten zwischen 5 und 25 s, wobei das Dismutationsverfahren eine Selektivität für die brauchbaren Produkte HCFC-123 und HCFC-125 von mehr als 98% hat.
2. Verfahren zur Herstellung von HCFC-123 nach Anspruch 1, worin das Aluminiumfluorid ein Aluminiumoxid-Fluorierungsprodukt mit einem Fluorgehalt von nicht weniger als 90%, vorzugsweise nicht weniger als 95%, der Stöchiometrie ist.
3. Verfahren zur Herstellung von HCFC-123 nach den Ansprüchen 1 und 2, in welchem der Träger 100 Gew.-% AlF_3 in gamma-Form ist.
4. Verfahren zur Herstellung von HCFC-123 nach den Ansprüchen 1 bis 3, in welchem das Chromoxid in Gegenwart von Oxyfluorid, Fluorid und Oxychlorid vorliegt.

Revendications

1. Procédé de préparation de HCFC-123 ayant une teneur en oléfines inférieure à 10 ppm consistant en la dismutation du HCFC-124 gazeux par mise en contact avec un catalyseur qui consiste essentiellement en oxyde de chrome trivalent (Cr_2O_3) supporté sur du fluorure d'aluminium, à des températures comprises entre 180° et 220°C, et avec des durées de contact comprises entre 5 et 25 secondes, dans lequel ledit procédé de dismutation donne lieu à une sélectivité en produits utiles HCFC-123 et HCFC-125 supérieure à 98%.
2. Procédé de préparation de HCFC-123 suivant la revendication 1, dans lequel le fluorure d'aluminium est le produit d'une fluoration d'alumine, présentant une teneur en fluor qui n'est pas inférieure à 90%, de préférence qui n'est pas inférieure à 95% exprimés par rapport à la stoechiométrie.
3. Procédé de préparation de HCFC-123 suivant les revendications 1 et 2, dans lequel le support est de l' AlF_3 à 100% en poids dans la forme gamma.
4. Procédé de préparation de HCFC-123 suivant les revendications 1 à 3, dans lequel l'oxyde de chrome est en présence d'oxyfluorure, de fluorure et d'oxychlorure.

THIS PAGE BLANK (USPTO)